

A self-organized critical model of rearranging hydrogen-bonded network in ice

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A dynamical four-vertex model of rearranging hydrogen-bonded network in ice, with a dynamics similar to the Grotthuss mechanism, is proposed. The model qualitatively explains the unusually high proton-conductivity in ice. It also serves as an interesting example of self-organized criticality with a non-conservative dynamics. The model is solved on a linear chain and its steady state is determined. Using numerical simulations, the model is further studied on a square lattice, and it is observed that it relaxes by three different avalanches, each of which follows a simple finite-size scaling.

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An isolated water molecule can be said to be well understood because its properties, as observed in experiments, can be described by the first principles quantum mechanical calculations. However, when a large number of these molecules form liquid-water or ice, our ability to predict their properties becomes limited [1]. In fact, water has a large number of anomalous properties [2], amongst which the unusually high mobility of H^+ has attracted a lot of attention. The observed value of the mobility in bulk ice [3] or water-filled narrow pores [4] are comparable to the electronic mobilities in some semiconductors. Conduction of H^+ is also fundamental to a myriad of processes ranging from ATP synthesis to electrical power generation in hydrogen fuel cells.

The generally accepted idea is that the hydrogen-bonded network of water molecules provides conduction pathways to H^+ , which migrates via Grotthuss mechanism [5]. In this, an extra H^+ in the network appears as a hydronium ion (H_3O^+), which translocates by hopping of H^+ across the hydrogen bonds (Fig. 1). This movement is hindered by the broken hydrogen bonds in the network (now on referred to as defects), which themselves migrate by rotation of the water molecules. The rotation of the molecules is slower than the hopping of H^+ and is therefore the rate limiting step [5]. However, a comparison of the mobility of H^+ , determined experimentally, with that of the defects, estimated assuming a simple diffusion, shows that the former is much higher at low temperatures [6]. We show that this problem can be qualitatively resolved if one considers a long-range correlation in the hydrogen-bonded network. While presence of this correlation has been experimentally observed and its importance envisioned [7], a clear understanding is still missing. In this letter, we propose a model of rearranging hydrogen-bonded network, with a Grotthuss-type dynamics, which exhibits a long-range correlation in its steady state. This correlation in the network increases the mobility of the defects, and a long distance transport of these occurs with a non-zero probability. We solve this model on a linear chain and determine its steady

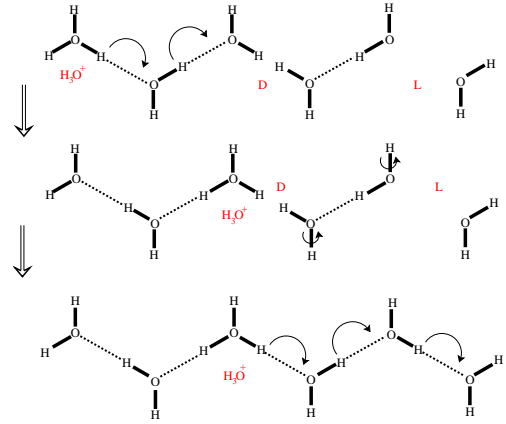


FIG. 1. (Color online) A schematic of H^+ transport by the Grotthuss mechanism. The hydronium ion and the two types of broken bonds, D and L are shown by red letters. The hopping of H^+ and the rotation of molecules around an O-H axis are indicated by arrows.

state. Further, using numerical simulations on a square lattice, we show that, in the steady state, the probability distribution of long distance transport of the defects can be described by a linear combination of simple scaling forms.

The model is interesting *per se*, as it provides a theoretical example of Self-Organized Criticality (SOC) with non-conservative dynamics. The existence of non-conservative models of SOC has been long debated. The much studied models, like the forest fire model [8], the Olami-Feder-Christensen model in the non-conservative limit [9] and their variants are known to be non-critical [10]. The non-conservative sandpile model studied by Pruessner and Jensen [11] is critical in the infinite volume limit, but lacks a well defined finite-size scaling, unless a control parameter is fine-tuned [10]. The model we propose does not have any conserved quantities. When slowly driven, it exhibits a scale invariance, following a finite-size scaling, without any apparent fine tuning of parameters. As the model shares some features with the

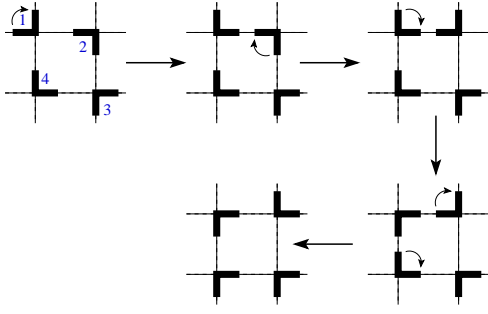


FIG. 2. An illustration of the relaxation, started by rotating the molecule at the top-left site of a 2×2 lattice. The covalent O-H bonds are denoted by solid lines, and the rotation of molecules are indicated by arrows. The four orientations of a molecule are denoted by 1, 2, 3 and 4.

well known ice model [12] of equilibrium statistical mechanics and also with the sandpile model of SOC [13], we call it *the icepile model*.

We define the model on a square lattice with open boundaries (Fig. 2). Every site on the lattice is occupied by an oxygen atom. Two hydrogen atoms are connected to each site by covalent bonds and they are always at right angles to each other. This is a special case of the standard ice model, with only four out of the six orientations allowed, *i.e.*, the orientations where two hydrogens are diametrically opposite to each other, are not allowed.

Any orientational arrangement of the molecules may have empty edges or edges occupied by two hydrogen atoms. These are known as L- and D-defects [5], respectively. Hydrogens in the neighboring molecules interact via repulsive electrostatic interaction, and the D-defects cost energy. Let the energy be U for a D-defect, and zero for the singly- or un-occupied edges. Further, to specify the orientations of the water molecules, we introduce a set of variables $\tau_{i,j}$ such that $\tau_{i,j} = 1$, when a hydrogen atom from the i th site is along the i - j edge, and $\tau_{i,j} = 0$, otherwise. The energy of a configuration is then described by an effective Hamiltonian

$$\mathcal{H} = \frac{U}{2} \sum_{\langle i,j \rangle} \tau_{i,j} \tau_{j,i}, \quad (1)$$

where the angular brackets indicate that i and j are nearest neighbors, and $\tau_{i,j} = 0$ for sites outside the boundary. The equilibrium properties corresponding to this Hamiltonian are easy to determine, if we represent each orientation of a water molecule by a pair of Ising-spins, taking up or down and left or right orientations. This breaks the system into mutually uncoupled horizontal and vertical linear chains of Ising-spins, which is exactly solvable.

As mentioned before, the translocation of the defects determines the effective mobility of H^+ , and this is what we study in the non-equilibrium steady state of our model. We assume the configurations with D-defects as

unstable. In an ice crystal, the defects are formed mostly by thermal excitations and their diffusion takes place by the reorientation of water molecules [5]. We generate the defects by forcibly reorienting a randomly chosen molecule by 90° clockwise rotation, calling it an *external drive*. If this creates a D-defect, we use the following odd-even update rule to relax the configuration (see Fig. 2): We divide the lattice into two sub-lattices according to the parity of $x+y$, where x and y are the Cartesian coordinates of a site. We pick one sub-lattice and select all sites on it contributing to a D-defect and simultaneously rotate the corresponding water molecules by 90° clockwise. This may create or annihilate D-defects and/or move them by one lattice unit. We do the same for the other sub-lattice and repeat until the system reaches a stable configuration. At this stage we again disturb the system by forcibly rotating another randomly chosen molecule and repeat.

We refer to a complete relaxation process, starting from the driving to reaching a stable configuration, as an avalanche. The number of D-defects is not conserved in an avalanche. The reorientation of the molecules in a relaxation step may create more D-defects which move on the lattice until they meet an empty edge or the lattice boundary, where they annihilate. Unlike the conserved sandpile models, the activity during a relaxation is not coupled to any conserved quantities.

There are a large number of stable configurations, all of which appear with a non-zero probability in the steady state. This can be verified from the fact that the configuration with all water molecules in the same orientation can be reached from any stable configuration, and *vice versa*. In a stable configuration, each row and column in the lattice has at most one empty edge whose positions uniquely determine the configuration. For each row with L sites, there are $L+1$ ways of placing the empty edge (we consider the configuration with no empty edges as the one with empty edges outside the lattice). Then for an $L \times M$ lattice, there are

$$\Omega_{square} = (L+1)^M (M+1)^L \quad (2)$$

ways of placing the empty edges, thus, so many stable configurations.

We first study an $L \times 1$ chain and show that all the $2^L (L+1)$ stable configurations are equally probable in the steady state. Let $|C\rangle$ be a stable configuration. Define an operator a_i by the relation $a_i|C\rangle = |C'\rangle$, where $|C'\rangle$ is the configuration reached by driving at site i of the chain in configuration $|C\rangle$, and relaxing. The D-defect created by the driving, moves toward the empty edge and vanishes by annihilating with it. It is always the molecule at the site next to the empty edge, which rotates last. For the present case, let that site be j . We define an operator R , corresponding to the reflection of the system across a line parallel to the chain, which maps any allowed configuration to another unique allowed configuration. Then it

can be shown that there exists an avalanche corresponding to the equation $a_j R[C'] = R[C]$. Similar argument applies for all the driving operators, implying that they all have an inverse. Thus the Markov evolution satisfies the pairwise balance [14], and hence the steady state is equally probable.

Let s be the total number of 90° rotations of the water molecules in an avalanche, and $P(s, L)$ be the probability of such events on a linear chain of L sites. As noted, the D-defect generated by the driving moves toward the empty edge, and vanishes by annihilating with it. All the sites in its path rotate at least once. If the driving site is on the right of the empty edge, then, before relaxation, the sites in between are either in state 3 or 4 (Fig. 2). For the configurations where all these sites are in state 3, the corresponding water molecules rotate just once. If any of these sites are in state 4, then, each of them individually increases the total number of rotations by 2. Thus, effectively, the sites in state 3 and 4 contribute $s = 1$ and $s = 3$, respectively. A similar argument applies for the driving sites on the left of the empty edge. From this it is easy to show that the probability

$$P(s+1, L) = \sum_{k=0}^{\lfloor s/3 \rfloor} \binom{s-2k}{k} 2^{2k-s} \frac{L-(s-2k)}{L(L+1)} + \frac{1}{2} \delta_{s,0}, \quad (3)$$

where $\lfloor x \rfloor$ is the largest integer less than or equal to x and $\delta_{i,j}$ is the Kronecker delta, which corresponds to the fact that half of the times the driving does not create any D-defect. For a large s , the expression reduces to a simple scaling form

$$P(s, L) \simeq L^{-1} g(s/L), \quad (4)$$

where $g(x) = 2^{-1}(1 - x/2)$.

Let us now consider an $L \times L$ lattice. Our numerical studies show that, in the steady state, the empty edges are more likely to be found near the center of the lattice. This implies that the stable configurations in the steady state are not equally probable.

On this lattice there are three types of avalanches. A schematic of these avalanches are shown in Fig. 3. In type I, the activity is confined along a single row or a column. In the other two types, the activity spreads on a two-dimensional area. In one of these, the activity moves like a single wave crossing the sites in its path only once, and the water molecules rotate less than five times. This is the type II avalanche. In the other, the waves move back and forth on the lattice, until the system reaches a stable configuration. This is the type III avalanche. The number of rotations increases for the sites which are away from the boundary of the affected region, and has a maximum value of the order L . Then the cutoff in the total number of rotations, s , in an avalanche, scales as L , L^2 and L^3 for the three types of avalanches, respectively. In such a case, the probability distribution is expected to

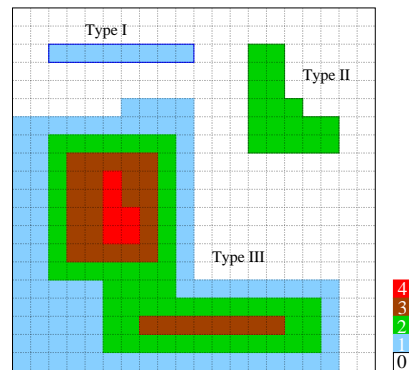


FIG. 3. (Color online) A schematic of the affected regions in the three types of avalanches on a 20×20 lattice. Each colored box is a unit cell of the lattice. Different colors represent, different number of rotations per site.

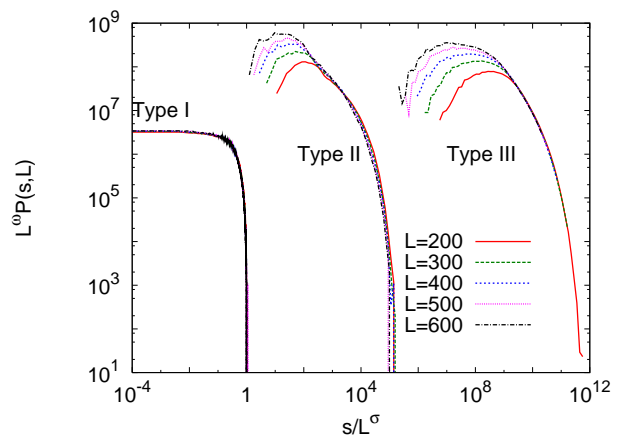


FIG. 4. (Color online) The scaled size distribution plots of the three avalanches. The exponents for the type I, II and III avalanches are $\sigma = 1, 2, 3$, and $\omega = 9/8, 11/4, 3$, respectively. For a better view, the graphs for type II and III have been shifted by 10^5 and 10^{12} units, on the x-axis.

have a scaling form

$$P(s, L) = \frac{1}{L^\alpha} f\left(\frac{s}{L}\right) + \frac{1}{L^\beta} g\left(\frac{s}{L^2}\right) + \frac{1}{L^\nu} h\left(\frac{s}{L^3}\right), \quad (5)$$

with the scaling functions f, g and h , which vanish as their argument approaches $\mathcal{O}(1)$. A similar linear combination of simple scaling forms was found in a few other models [15, 16].

We have analyzed our Monte-Carlo simulation results for five different values of L , each averaged over 10^6 trials. The best data collapse of the numerical results is obtained for the values $\alpha \simeq 9/8$, $\beta \simeq 11/4$ and $\nu \simeq 3$ (Fig. 4). This implies that the probability of type I and type II avalanches decreases as $L^{-1/8}$ and $L^{-3/4}$, for large L . This is consistent with the numerical results in Fig. 5. Thus, in the thermodynamic limit, there will be mostly type III avalanches.

The geometry of the lattice is important in deciding the

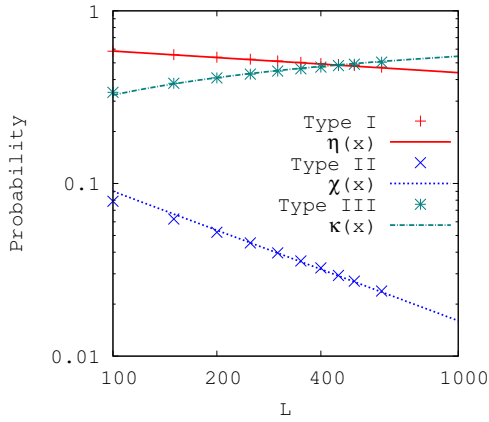


FIG. 5. (Color online) Probability of different types of avalanches. The fitting functions are $\eta(x) = 1.04/x^{1/8}$, $\chi(x) = 2.85/x^{3/4}$ and $\kappa(x) = 1 - \eta(x) - \chi(x)$, for type I, II and III, respectively.

criticality of the steady state. To see this, we consider a straight-forward generalization of our model on to other lattices. First we consider a three-coordinated Caley tree. Using an argument similar to the one-dimensional chain, one can see that all the stable configurations are equally probable in the steady state. Then using the tree structure of the lattice, it is easy to show that the probability of an avalanche in which r distinct water molecules rotate, has a form $2^r \exp(-kr/\log v)$, where v is the number of vertices on the Caley tree and k is a numerical constant. Then the steady state is not critical. On any other three-coordinated lattice, e.g., hexagonal lattice, there will be lesser freedom for the water molecules. However, on lattices like square or Kagome lattice, where each site is connected to four neighbors, the probability distribution has a power-law tail, implying that the steady state is critical. On a lattice with coordination number greater than four, e.g., cubic lattice, the water molecules become stable more easily, and the probability of getting large avalanches decreases exponentially.

In an ice crystal, the water molecules are arranged on a four-coordinated diamond-like lattice. Such a lattice is more like the Kagome lattice, and the steady state of the icepile model is expected to be critical. Although the dynamics of the model in its present form is not very realistic (a more careful modeling of the intra-molecular interaction and the dynamics is required), it does show an important qualitative property of ice – there is a long-range correlation in the hydrogen-bonded network [7].

In the Grotthuss mechanism, because the molecular re-orientation is slower than the H^+ hopping, the effective mobility of H^+ is limited by that of the defects. However, when the defect-mobility was estimated [6] using experimental value of water rotation time [17] and assuming a *simple diffusion*, it was found that it is much

less compared to the experimental value of H^+ mobility, at low temperatures. This discrepancy can be resolved qualitatively, staying within the Grotthuss formalism, if one considers the long-range correlation in the hydrogen-bonded network. The correlated walk on the network increases the mobility of the defects significantly, and this in turn increases the mobility of H^+ .

In *summary*, we have proposed a dynamical model of the hydrogen-bonded network in ice, the steady state of which, in the slow driving limit, has a long-range correlation. Ignoring this correlation in the study of proton conduction in real ice, can be misleading. The model is also an example of SOC with non-conservative dynamics. Another important aspect of the model is that its dynamics is non-abelian, *i.e.*, the final configuration depends on the order in which the system is driven. All the known undirected models of SOC with exact solutions are abelian [13]. There are only a handful of analytical results available for the non-abelian models [18, 19], but those are all in the special limit, where the dynamics essentially becomes abelian. In fact, even the one-dimensional non-abelian models also are highly non-trivial. We solved the icepile model in one dimension, and determined its steady state. We also calculated the exact number of recurrent configurations on a square lattice. A similar calculation is possible on a Kagome lattice, and it can be shown that the number of recurrent configurations

$$\Omega_{Kagome} = L!^2 \times 4^{2L} (2L + 1)^L, \quad (6)$$

on a $2L \times 2L$ Kagome lattice with open boundaries.

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